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(54) Germicidal composition.

(57) A germicidal composition is disclosed which comprises a solvent containing at least 50 % by weight of a stabilizing liquid selected from 3-methyl-3-methoxybutyl alcohol and ethylene glycol diacetate, and an isothiazolone compound dissolved in the solvent.

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GERMICIDAL COMPOSITION

This invention relates generally to a germicide suitable for preventing growth of various germs such as yeasts and filamentous fungi in industrial water such as waste water from pulp mills or cooling water for heat exchangers and, more specifically, to a germicidal composition of the above-mentioned type which is stable and has an improved shelf life.

In industrial water such as waste water from paper making steps in pulp-related industries and recirculating cooling water used in various mills, microorganisms such as germs, fungi and bacteria are apt to grow to form slimes which cause various problems. To cope with this, various germicides have been proposed and some of them are actually used for destroying germs or preventing growth of germs in various fields. Among various germicides, an isothiazolone compound is known to be especially effective in preventing the occurrence of slimes. Isothiazolone compound containing germicides are generally stored, transported or placed on sales in the form of concentrated solutions. Glycols, ketones or ethers are generally used as solvents for such germicidal solutions.

It has been found, however, that isothiazolone compounds in such solutions are not stable and, therefore, the germicidal activity of such solutions is gradually degraded when stored for a long period of time.

The present invention has been made with the above problem of the conventional germicides in view and is contemplated to provide an isothiazolone-type germicide having an improved shelf life. In accordance with the present invention there is provided a composition in the form of a solution, comprising:

an isothiazolone compound; and

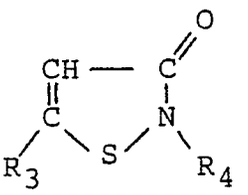
a solvent containing at least 50 % by weight of a stabilizing liquid having the following general formula:

$R_1 - CH_2 - CH_2 - O - R_2$

wherein R_1 stands for $-C(CH_3)_2OCH_3$ or $-OCOCH_3$ and R_2 stands for hydrogen or $-COCH_3$ with the proviso-that when R_1 is $C(CH_3)_2OCH_3$ R_2 is hydrogen and that wnen R_1 is $-OCOCH_3$ R_2 is $-COCH_3$.

The present invention will now be described in detail below.

Any isothiazolone compound may be used for the purpose of the present invention as long as it has a germicidal activity. If desired, a mixture of two or more isothiazolone compounds may be used. Particularly suited are isothiazolone compounds represented by the following general formula:



wherein R_3 stands for hydrogen or halogen and R_4 stands for hydrogen or alkyl. Illustrative of suitable isothiazolone compounds are 2-methyl-3-isothiazolone, 5-chloro-2-methyl-3-isothiazolone, 2-octyl-3-isothiazolone, 2-ethyl-3-isothiazolone and mixtures thereof. Complexes of isothiazolones, such as calcium chloride complexes, magnesium nitrate complexes and iron chloride complexes, may also be used, though the use of free form isothiazolones is preferred.

The present invention is characterized by using a specific stabilizing liquid as shown by the above general formula as a major component of a solvent for the above isothiazolone compounds. It is important that the solvent should contain at least 50 % by weight, preferably 60 % by weight of the stabilizing liquid in order to attain the object of the present invention.

If desired, an auxiliary organic solvent may be used in conjunction with the stabilizing liquid. Examples of such auxiliary solvents include monohydric alcohols such as benzyl alcohol, butanol and isopropyl alcohol; glycols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol and propylene glycol; ethers such as ethylene glycol mono(or di)alkyl ether, 1,4-dioxane, dibenzyl ether and propylene oxide; esters such as ethylene glycol monoacetate, alkyl acetates and alkyl adipates; hydrocarbons such as dodecylbenzene and psuedocumene, amides such as dimethylformamide; ketones such as methyl isobutyl ketone; and dimethylsulfoxide. The amount of such an auxiliary solvent should not exceed 50 % by weight.

The solvent containing the above stabilizing liquid and, optionally, the above auxiliary solvent, is generally used in an amount so that the concentration of the isothiazolone compound is 0.1-70 % by weight, preferably 0.4-50 % by weight, based on the total weight of the isothiazolone compound and the solvent.

If desired, isothiazolone compounds may be used in conjunction with one or more other germicides such as 4,5-dichloro-1,2-dithiole-3-one, 2,2-dibromo-3-nitrilepropionamide, 2,2-dibromo-2-nitroethanol, methylenebisthiocyanate, 1-chloroben-

zaldoxime acetate and bis(bromoacetoxy)butene.

Solutions of an isothiazolone compound in the above stabilizing liquid-containing solvent are excellent in stability and the isothiazolone compound in the solution is prevented from decomposing for a long period of time. Thus, degradation of germicidal activity during storage or transportation is effectively prevented, so that the solution is advantageously used as a germicide or a raw material for the production of germicides.

The following examples will further illustrate the present invention.

Examples 1-17

One or more of the isothiazolone compounds shown in Table 1 were dissolved in 3-methyl-3-methoxybutyl alcohol of the formula: CH_3O - C-$(CH_3)_2$ - CH_2 - CH_2 - OH or a mixed solvent composed of 3 methyl-3-methoxybutyl alcohol and an auxiliary solvent shown in Table 1. The amounts (parts by weight) of the isothiazolone compounds, 3-methyl-3-methoxybutyl alcohol and the auxiliary solvents are also shown in Table 1.

In Table 1, the abbreviations are as follows:

Isothiazolone Compound :
ITZ-1: 5-Chloro-2-methylisothiazolone
ITZ-2: 2-Methylisothiazolone
ITZ-3: 2-Octylisothiazolone
Stabilizing Liquid :
MMB: 3-Methyl-3-methoxybutyl alcohol
Auxiliary Solvent :
EG: Ethylene glycol
DEG: Diethylene glycol
PG: Propylene glycol
DGME: Diethylene glycol monomethyl ether
MBK: Methyl isobutyl ketone
DBE: Dibenzyl ether
PO: Propylene oxide
PEG: Polyethylene glycol (molecular weight: 400)

The thus prepared solutions were then allowed to stand at 40 °C for 30 days. The concentration (C) of the isothiazolone compound or compounds in each solution was measured 5, 10, 20 and 30 days after the preparation thereof to evaluate the stability thereof in terms of "survival rate" calculated from the following equation:

Survival rate = $\frac{C}{C_0} \times 100$ %

wherein C represents the measured concentration and C_0 represents the initial concentration. The results are also shown in Table 1.

Table 1

Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Isothiazolone																	
ITZ-1	20			15	20	20	20	20	20	20	20	20	15	15		5	5
ITZ-2		20		5									5	5			
ITZ-3			20												20		
Stabilizing Liquid																	
MMB	80	80	80	80	50	50	50	50	50	50	50	50	50	70	70	95	60
Auxiliary Solvent																	
EG					30								30	10			35
DEG						30											
PG							30								10		
DGME								30									
MBK									30								
DBE										30							
PO											30						
PEG												30					
Survival Rate (%)																	
5 days	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
10 days	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
20 days	100	100	100	100	98	98	95	98	93	96	98	98	98	100	100	100	99
30 days	99	100	100	100	95	96	92	96	88	91	96	96	97	98	98	100	98

Comparative Examples 1-17

The procedures of the above examples were repeated in the same manner as described except that the amounts of 3-methyl-3-methoxybutyl alcohol and the auxiliary solvents were changed as shown in Table 2. The results are also summarized in Table 2.

Examples 18-34

Examples 1-17 were repeated in the same manner as described except that ethylene glycol diacetate (EGD) of the formula:
$H_3CCO - O - CH_2 - CH_2 - O - COCH_3$
was used as the stabilizing liquid in place of 3-methyl -3-methoxybutyl alcohol. The results are shown in Table 3.

Comparative Examples 18-25

Comparative Examples 10-17 were repeated in the same manner as described except that ethylene glycol diacetate (EGD) was used as the stabilizing liquid in place of 3-methyl-3-methoxybutyl alcohol. The results are shown in Table 4 together with those of Comparative Examples 1-9.

Table 2

Comparative Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Isothiazolone																	
ITZ-1	20			15	20	20	20	20	20	20	20	20	15	15		5	5
ITZ-2		20		5									5	5			
ITZ-3			20												20		
Stabilizing Liquid																	
MMB										30	30	30	30	10	10		10
Auxiliary Solvent																	
EG	80	80								50			50	70		95	85
DEG				80													
PG			80												70		
DGME					80						50						
MBK						80											
DBE							80					50					
PO								80									
PEG									80								
Survival Rate (%)																	
5 days	86	99	100	98	85	65	85	50	63	98	96	100	100	96	100	90	100
10 days	75	88	96	80	24	16	80	2	8	86	86	76	90	82	92	66	90
20 days	69	54	65	65	13	5	52	0	0	70	75	46	32	26	62	34	62
30 days	3	25	45	12	2	0	9	0	0	6	3	2	0	0	21	6	10

Table 3

Example No.	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
Isothiazolone																	
ITZ-1	20			15	20	20	20	20	20	20	20	20	15	15		5	5
ITZ-2		20		5									5	5			
ITZ-3			20												20		
Stabilizing Liquid																	
EGD	80	80	80	80	50	50	50	50	50	50	50	50	50	70	70	95	60
Auxiliary Solvent																	
EG					30								30	10			35
DEG						30											
PG							30								10		
DGME								30									
MBK									30								
DBE										30							
PO											30						
PEG												30					
Survival Rate (%)																	
5 days	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
10 days	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
20 days	100	100	100	100	100	100	98	100	93	98	100	100	100	100	100	100	99
30 days	99	100	100	100	95	96	92	96	90	93	98	98	97	98	98	98	98

Table 4

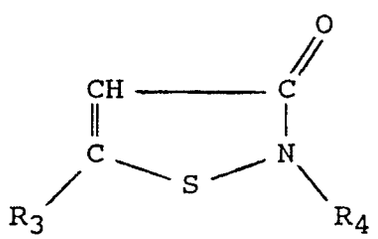
Comparative Example No.	1	2	3	4	5	6	7	8	9	18	19	20	21	22	23	24	25
Isothiazolone																	
ITZ-1	20			15	20	20	20	20	20	20	20	20	15	15		5	5
ITZ-2		20		5									5	5			
ITZ-3			20												20		
Stabilizing Liquid																	
EGD										30	30	30	30	10	10		10
Auxiliary Solvent																	
EG	80	80								50			50	70		95	85
DEG				80													
PG			80												70		
DGME					80						50						
MBK						80											
DBE							80					50					
PO								80									
PEG									80								
Survival Rate (%)																	
5 days	86	99	100	98	85	65	85	50	63	96	96	96	96	100	100	90	96
10 days	75	88	96	80	24	16	80	2	8	80	90	74	86	88	88	66	82
20 days	69	54	65	65	13	5	52	0	0	62	70	40	36	36	52	34	50
30 days	3	25	45	12	2	0	9	0	0	2	4	0	0	0	10	6	6

Claims

1. A composition comprising:
a solvent which comprises at least 50% by weight of a stabilizing liquid having the following general formula:
$R_1 - CH_2 - CH_2 - O - R_2$
wherein R_1 stands for $-C(CH_3)_2OCH_3$ or $-OCOCH_3$ and R_2 stands for hydrogen or $-COCH_3$ with the proviso that when R_1 is $-C(CH_3)_2OCH_3$ R_2 is hydrogen and that when R_1 is $-OCOCH_3$ R_2 is $-COCH_3$, and
an isothiazolone compound dissolved in said solvent.

2. A composition according to Claim 1, wherein the isothiazolone compound is present in an amount of 0.1-70% by weight.

3. A composition according to Claim 1 or Claim 2, wherein said isothiazolone compound is at least one compound selected from those represented by the following general formula:



wherein R_3 stands for hydrogen or halogen and R_4 stands for hydrogen or alkyl, and complexes thereof.

4. A composition according to any preceding claim, wherein the content of said stabilizing liquid in said solvent is at least 60% by weight.

5. A composition according to any preceding claim, further comprising one or more germicide selected from the group consisting of 4,5-dichloro-1,2-dithiole-3-one, 2,2-dibromo-3-nitrilepropionamide, 2,2-dibromo-2-nitroethanol, methylenebisthiocyanate, 1-chlorobenzaldoxime acetate and bis(bromoacetoxy)butene.

6. A composition according to any preceding claim, wherein the solvent comprises one or more auxiliary organic solvents.